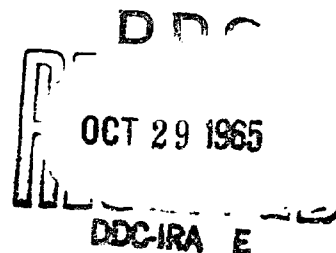ARL 65-169
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THE CATALYTIC DECOMPOSITION OF NITROUS OXIDE AND THE THERMAL DECOMPOSITION OF NITROGEN DIOXIDE

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AUGUST 1965

FOREWORD

This interim technical documentary report was prepared by E. Stokes Fishburne, Daniel M. Bergbauer and Rudolph Edse of the Department of Aeronautical and Astronautical Engineering of the Ohio State University on Contract No. AF 33(657)-8951, Project 7065, Aerospace Simulations Techniques Research. The research on this task was administered under the direction of the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force, with Mr. John Goresh, Fluid Dynamics Facilities Laboratory, as contract monitor.

This report covers one phase of the investigation on Contract AF 33(657)-8951.

ABSTRACT

The reaction between atomic oxygen and nitrous oxide has been studied at temperatures ranging from $1500^{\circ}K$ to $2100^{\circ}K$. The atomic oxygen in this study was generated by either the thermal decomposition of nitrogen dioxide or the thermal decomposition of ozone. To determine the amount of atomic oxygen released in the thermal decomposition of nitrogen dioxide it was necessary to study this decomposition in detail. This study was conducted also at temperatures ranging from $1500^{\circ}K$ to $2000^{\circ}K$ and over a wide range of concentrations and pressures. The reaction rates obtained for the various steps in the decomposition of nitrogen dioxide are in general agreement with those obtained by other investigators. The reaction of nitrous oxide in the presence of nitrogen dioxide with argon as the diluent was studied to determine if the oxygen released in the decomposition of nitrogen dioxide would accelerate the decomposition of nitrous oxide. No noticable acceleration was observed.

Many experiments were conducted with a nitrous oxide mole fraction of 0.02 and ozone mole fractions varying between 0.005 and 0.06. In these experiments the diluent was molecular oxygen. The presence of atomic oxygen definitely produced an increase in the rate of decomposition of nitrous oxide. It is found that the reaction between atomic oxygen and nitrous oxide is pressure dependent. It is shown that the different rate constants obtained by other investigators may be reasonably explained on the basis of a pressure dependent step in the reaction mechanism.

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LIST OF SYMBOLS

(C)	Concentration of species
t	Time
E_{act}	Activation energy
T	Absolute temperature
k_j	Reaction rate constant for reaction j
K_{exp}	Experimental reaction rate constant based on first order reaction
M	Inert species
R	Universal gas constant
A	Frequency factor
m_{O_3}	Molecular weight of ozone

SECTION I. INTRODUCTION

The possibility of using nitrous oxide as a working fluid in hypersonic wind tunnels depends to a large extent on whether the decomposition of nitrous oxide can be reliably controlled. As a result of recent work (Ref. 1-4) the decomposition rate of nitrous oxide is known fairly accurately to temperatures of about $2200^{\circ}K$. The gaseous mixtures employed in these experiments consisted mainly of argon, air, oxygen or nitric oxide with a small percentage of nitrous oxide. The use of the various mixtures of diluent and nitrous oxide was necessary in order that a relatively constant temperature of the gas sample could be maintained as the decomposition proceeds. If nitrous oxide is used in hypersonic wind tunnels, the amount of nitrous oxide to produce the oxygen to nitrogen ratio of air would be of the order of 55% of the total mixture.

The decomposition of nitrous oxide in a mixture containing a large amount of nitrous oxide is much more complicated than the decomposition studied in Ref. 1-4. As the nitrous oxide decomposes the heat released during the reaction increases the temperature of the gas which produces a faster decomposition rate, which releases more heat etc. until the gas appears to decompose instantly. Such a decomposition process is called a thermal explosion. In this situation the other gases which are present would contribute in varying degrees to the over-all decomposition rate of the nitrous oxide. For instance, the gases which are generated would be nitrogen, oxygen, atomic oxygen and nitric oxide. The rate of decomposition of nitrous oxide in nitrogen, oxygen and nitric oxide is known fairly well (Ref. 1). However, the effect of atomic oxygen on the decomposition process is not known very accurately at the temperatures above $1000^{\circ}K$. For a description of the decomposition process the reaction between the atomic oxygen and nitrous oxide should be studied in a more detailed manner. Furthermore, once the nitrous oxide has started to decompose the remaining nitrous oxide will decompose very rapidly due to the thermal explosion which follows.

With the use of nitrous oxide in wind tunnels a problem may arise as to the initiation of the nitrous oxide decomposition. The decomposition obviously must be initiated in the stagnation chamber and not in the heater section of the wind tunnel. If the decomposition is initiated in the heater section of the wind tunnel the subsequent rapid decomposition of nitrous oxide would release a large amount of heat resulting in a burnout of the heater section (Ref. 5). Therefore, the heater section should heat the nitrous oxide to a temperature just below that at which it begins to decompose rapidly. Then if the nitrous oxide can be made to decompose rapidly, by the addition of some type of catalytic gas, the ensuing rapid thermal decomposition would insure a complete decomposition of nitrous oxide in the stagnation chamber.

The catalyst should be gaseous and produce products which are either oxygen or nitrogen. According to low temperature data the rate of decomposition of nitrous oxide due to the reaction between nitrous oxide and atomic oxygen is somewhat faster than the thermal decomposition of nitrous oxide at temperatures below approximately $1400^{\circ}K$. Therefore, it appears possible that if atomic oxygen could be added by some means to the nitrous oxide at the exit of

the heater section then the resultant fast decomposition could initiate the over-all decomposition of the nitrous oxide. The main problem would be to introduce atomic oxygen into the system. Atomic oxygen may be introduced into the system by adding either ozone or possibly nitrogen dioxide. The effectiveness of nitrogen dioxide in providing oxygen atoms for the decomposition of nitrous oxide is somewhat questionable. To determine the effectiveness of nitrogen dioxide it is necessary to know the decomposition rate of nitrogen dioxide and the number of oxygen atoms that are released in these reactions. Thus we see that the reaction between atomic oxygen and nitrous oxide is important from the viewpoint of understanding and predicting the rate of decomposition of nitrous oxide in mixtures containing large quantities of nitrous oxide at high temperatures.

SECTION II. EXPERIMENTAL APPARATUS

The experimental apparatus employed in this study is essentially the same system discussed in detail in References 1 and 2. The measurement of the nitrogen dioxide decomposition was obtained by employing both infrared emission techniques and absorption of radiation between 3000Å and 6000Å. Nitrogen dioxide absorbs energy quite strongly in the visible region of the spectrum. Unfortunately, the intensity of the infrared radiation is fairly low. To obtain a sufficiently intense emission from the gas it was necessary to employ either a sodium chloride prism in the existing monochrometer or to employ a filter that transmits only the radiation between 3 and 4 microns. With the sodium chloride prism a much lower dispersion was produced. Thus the number of quanta per unit area at the exit of the monochrometer was increased so that larger signal to noise ratio was obtained.

However, when very low concentrations of nitrogen dioxide were studied it was found that even the use of the sodium chloride prism did not direct sufficient radiation on the detector to obtain reliable results. Therefore, an infrared filter was employed which transmitted only the radiation between 3 and 4 microns In this spectal region several infrared bands exist which can be used to study the radiation of nitrogen dioxide. To insure that the use of the 3 to 4 micron filter did not introduce other possible errors identical experiments were conducted and the data obtained with the 3 to 4 micron filter were compared with those obtained with the salt prism. The data agreed very well.

The rate of decomposition of nitrogen dioxide also was studied by employing the absorption of radiation between 3000Å and 6000Å. Since nitrogen dioxide absorbs very strongly in the region around 4300Å (Ref.6) the decomposition rate could be determined fairly accurately. However, more problems are encountered when the visible absorption techniques are employed instead of the infrared emission techniques. In the existing facility the signal to noise ratio for the visible absorption was not as good as that observed for the infrared emission. Furthermore, the reaction rates which were derived from the absorption in the visible region were slightly faster than those obtained when the infrared emission was employed.
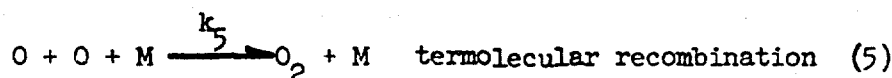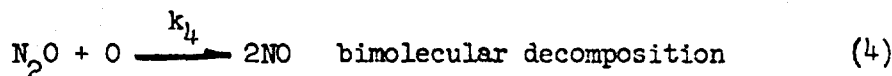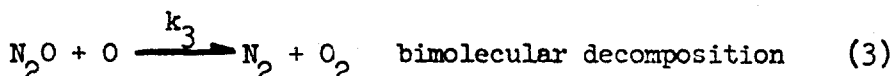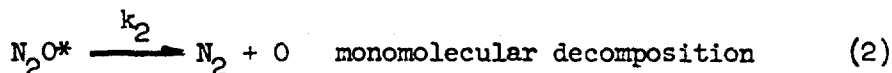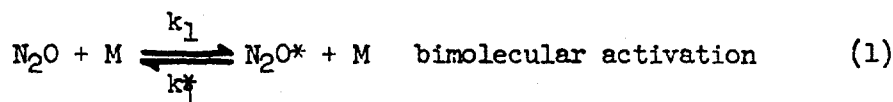
It was not necessary to study the decomposition of ozone since these decomposition rates are known quite accurately in the temperature region of interest. Therefore, in the study of the effects of the ozone on the decomposition of nitrous oxide only the radiation from the nitrous oxide molecule was monitored. The techniques employed were discussed in References 1 and 2.

The nitrogen dioxide employed in the study was obtained from the Matheson Company in the form of nitrogen tetroxide. The desired mixture of nitrogen dioxide, nitrous oxide and argon was determined on the basis of equilibrium between the nitrogen dioxide and nitrogen tetroxide with the data presented in Reference 7.

Ozone was prepared by passing oxygen through an ozonizer built specifically for this project (Figure 1). With this ozonizer and employing pure oxygen the maximum yield of ozone was 8% by volume.

SECTION III. THE REACTION BETWEEN ATOMIC OXYGEN AND NITROUS OXIDE

In the study of the reaction between atomic oxygen and nitrous oxide the following reactions are important.

$$N_2O + M \; \underset{k_1^*}{\overset{k_1}{\rightleftharpoons}} \; N_2O^* + M \quad \text{bimolecular activation} \qquad (1)$$

$$N_2O^* \; \xrightarrow{k_2} \; N_2 + O \quad \text{monomolecular decomposition} \qquad (2)$$

$$N_2O + O \; \xrightarrow{k_3} \; N_2 + O_2 \quad \text{bimolecular decomposition} \qquad (3)$$

$$N_2O + O \; \xrightarrow{k_4} \; 2NO \quad \text{bimolecular decomposition} \qquad (4)$$

$$O + O + M \; \xrightarrow{k_5} \; O_2 + M \quad \text{termolecular recombination} \qquad (5)$$

Instead of discussing the complete reaction mechanism of the decomposition process we shall discuss only the temperature regions in which each of the various reactions are of importance.

Reaction 5 is fairly independent of temperature but highly dependent on the species M. Reactions 1 and 2 have been discussed previously and the rate constants are given in References 1 and 2. Two rate constants are available in the literature for the combined reactions 3 and 4. When extrapolated to

the temperature region above 1300°K, these rate constants differ by a factor of about 40.

To investigate the rate of reactions 3 and 4 we must introduce a sufficient amount of atomic oxygen into the gas to make the decomposition of N_2O by reactions 3 and 4 faster than that by reactions 1 and 2. However, since the rates of reactions 3 and 4 depend on the first power of the atomic oxygen concentration and the recombination (reaction 5) depends on the square of the atomic oxygen concentration we are limited to a particular concentration region if we are to prevent substantial loss of atomic oxygen by reaction 5.

To these limitations we must add still another. This limitation is associated with the manner in which the atomic oxygen is introduced into the mixture. In our experiments the atomic oxygen is generated by the decomposition of either nitrogen dioxide or ozone. The concentration of oxygen atoms available for the reaction with nitrous oxide is limited by the reaction between atomic oxygen and ozone since this reaction proceeds very rapidly.
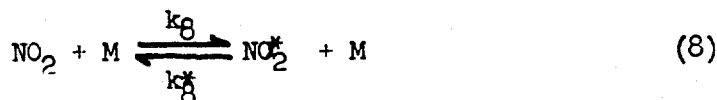
The decomposition of ozone is given by

$$O_3 + M \xrightarrow{k_6} O + O_2 + M \qquad (6)$$

$$O_3 + O \xrightarrow{k_7} 2O_2 \qquad (7)$$
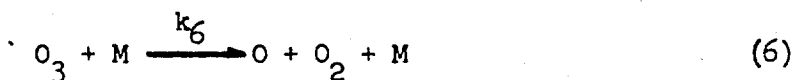
The rate constants, k_6 and k_7, are given in Reference 8. Using these rate constants we find that we must restrict our investigation to the temperature region above 1400°K. At temperatures lower than 1400°K only a small amount of atomic oxygen is formed since reaction 7 dominates.

SECTION IV. THE THERMAL DECOMPOSITION OF NITROGEN DIOXIDE - THEORY

To obtain a complete description of the thermal decomposition of nitrogen dioxide we must consider the reactions listed below

$$NO_2 + M \underset{k_8^*}{\overset{k_8}{\rightleftharpoons}} NO_2^* + M \qquad (8)$$

$$NO_2^* \xrightarrow{k_9} NO + O \qquad (9)$$

$$NO_2 + O \xrightarrow{k_{10}} NO + O_2 \qquad (10)$$

$$NO_2 + NO_2 \xrightarrow{k_{11}} 2NO + O_2 \qquad (11)$$

$$NO_2 + NO_2 \xrightarrow{k_{12}} NO_3 + NO \qquad (12)$$
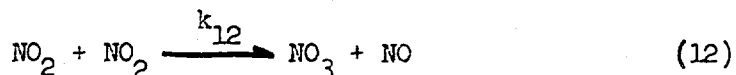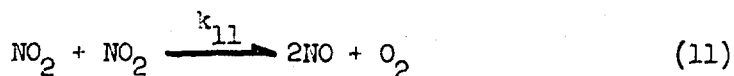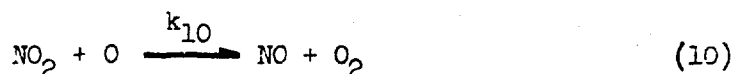
In reactions (9) through (12) we have not considered the reverse reaction since they should be very slow. According to eqns (8) through (12) the rate of decomposition of nitrogen dioxide may be given as

$$\frac{d(NO_2)}{dt} = -k_8 (NO_2)(M) + k_8^* (NO_2^*)(M) -k_{10} (NO_2)(O)$$
$$-2k_{11} (NO_2)^2 -2k_{12} (NO_2)^2 \qquad (13)$$

In our experiments we cannot distinguish between reactions 11 and 12. Therefore, we find it convenient to express these two reactions as

$$-2k_{11} (NO_2)^2 -2k_{12} (NO_2)^2 = -k_b (NO_2)^2 \qquad (14)$$

Thus equation 13 becomes

$$\frac{d}{dt} (NO_2) = -k_8 (M)(NO_2) + k_8^* (NO_2^*)(M) -k_{10} (NO_2)(O) -k_b (NO_2)^2 \qquad (15)$$

We have included a number of reactions which may not contribute in a significant manner as, for instance, the possibility of decomposition via an activated complex. Furthermore, we have assumed that reaction 10 between nitrogen dioxide and the atomic oxygen generated in reaction 9 may be significant in the overall decomposition process.

Assuming that the activated complex is in equilibrium with the normal nitrogen dioxide we can write

$$\frac{d(NO_2)}{dt} = -K_{exp} (NO_2) \qquad (16)$$

where

$$K_{exp} = \frac{k_8 (M)}{\frac{k_8^* (M)}{k_9} + 1} + k_{10} (0) + k_b (NO_2)$$ (17)

The rate constant K_{exp} is derived fron experimental measurements. The importance of the various reactions is obtained by measuring the contribution of each reaction to the observed value of K_{exp}. When eqn. (17) is divided by the total concentration (M) we obtain

$$\frac{K_{exp}}{(M)} = \frac{k_8}{\frac{k_8^* (M)}{k_9} + 1} + k_{10} \frac{(0)}{(M)} + k_b \frac{(NO_2)}{(M)}$$ (18)

The last term simply depends on the mole fraction of NO_2 in the mixture. Thus, to reduce the importance of reactions 11 and 12 we need only conduct experiments with low percentages of NO_2.

The contribution of the reaction between atomic oxygen and nitrogen dioxide is very difficult to evaluate from equation 18. This difficulty arises because of the recombination reaction

$$0 + 0 + M \xrightarrow{k_{19}} O_2 + M$$ (19)

For the rate of disappearance of atomic oxygen we have, neglecting molecular oxygen dissociation,

$$\frac{d(0)}{dt} = - 2k_{19} (M)(0)^2 - k_{10} (NO_2)(0)$$ (20)

For reaction 10 to dominate

$$k_{10} \frac{(NO_2)}{(M)} > 2k_{19} (0)$$ (21)

But this expression requires a knowledge of the values of k_{10} and k_{19}.

In order to determine the contribution of each reaction to the overall decomposition process we must:

1) Vary the ratio $(NO_2)/(M)$ to determine the role of reactions 11 and 12.

2) Vary the total concentration (M) to determine the role of reaction 8 and 9.

3) Investigate separately the reaction between atomic oxygen and nitrogen dioxide (reaction 10).

SECTION V. THE THERMAL DECOMPOSITION OF NITROGEN DIOXIDE -

EXPERIMENTAL RESULTS

The thermal decomposition of nitrogen dioxide was investigated in the temperature region between 1400°K and 2100°K. The total gas concentration was varied between 0.057 x 10⁻⁴ mole/cc and 0.90 x 10⁻⁴ moles/cc employing argon as the diluent. The mole fraction of nitrogen dioxide was varied from 0.005 to 0.03. The results of these experiments are shown in Figures 2-5 which represent data obtained behind both incident and reflected shock waves. A duplication in data was obtained by employing these two shock waves in order that any effects introduced by the reflected shock wave may be ascertained (Ref. 11). No discrepancies were observed.

In the graphs the quantity K_{exp}/M is plotted versus the inverse of the temperature. This particular method of data presentation was employed as a means of indicating whether the reaction is primarily bimolecular or monomolecular. Furthermore, the use of K_{exp}/M permits e rapid evaluation of the various contributions shown in eqn. 18. For a truly bimolecular reaction the measurement of K_{exp} for various total gas concentrations, but at a given nitrogen dioxide mole fraction, should lead to a straight line for the graph of $\ln(K_{exp}/M)$ versus T^{-1}. On the other hand, if the decomposition is more complex, the points would not form a straight line. From the graphs we find that the data do not lie on a straight line. However, the deviations from the straight line are small. At the lower total concentrations the points form almost a straight line indicating a bimolecular reaction. However, as the total concentration is increased the reaction appears to become more complex.

A very careful check of experimental procedures was undertaken to determine if any of the assumptions employed at the low concentrations would not be valid at the higher concentrations. The most obvious assumption is that the gas is optically thin in the infrared region. In other words, the assumption is made that the gas does not absorb any of its own radiation. If the gas begins to absorb its own radiation the reaction rates which were measured from the decrease in the radiation intensity would be somewhat slower than the actual rates. Radiation from a Nernst glower was passed through the shock heated gas to determine the extent of self absorption. The amount of absorption under the most extreme conditions was negligible. We, therefore, reached the conclusion that the observed rates were real and not due to the manner in which the data were evaluated. Furthermore, the decomposi-

tion rate also was determined by employing absorption and emission of radiation by nitrogen dioxide in the region 3000Å - 6000Å with essentially the same results.

At this time the most obvious explanation of the slower rates at the higher concentrations would be the effects of the unimolecular decomposition of the activated complex or the reaction between atomic oxygen and nitrogen dioxide or both. At the higher gas concentrations the recombination of oxygen atoms may compete with the reaction between atomic oxygen and nitrogen dioxide. At the present time we shall neglect the effects of these two reactions in our discussion.

Due to the rather limited range of nitrogen dioxide mole fractions employed in this study it was difficult to determine the contribution of reactions 11 and 12 without prior knowledge of their reaction rates. Rosser and Wise (Ref. 12) studied these two reactions in the temperature range between $600^{\circ}K$ and $1000^{\circ}K$ and obtained

$$k_{11} = 2 \times 10^{12} \exp(-26,900/RT) \tag{22}$$

$$k_{12} = 3.9 \times 10^{11} \exp(-23,900/RT) \tag{23}$$

Combining these two expressions into one rate constant, given by eqn. 14, we have

$$k_b = 4.1 \times 10^{12} \exp(-25,700/RT) \tag{24}$$

In our experimental analysis we shall use this activation energy but shall choose the best value of the frequency factor which will provide a good fit for the experimental data.

The reaction rate constant given by eqn. 8 has been determined by Huffmann and Davidson (Ref. 9) and by Hiraoka and Hardwick (Ref. 10). The activation energies given by these investigators are approximately 65,000 cal/mole. They obtained this activation energy for the low mole fractions of nitrogen dioxide. In one series of experiments we obtained an activation energy of approximately 58,000 cal/mole at low mole fractions of nitrogen dioxide and low overall concentrations. The activation energy decreased when larger nitrogen dioxide mole fractions were employed. On the other hand, the activation energy decreased as the total concentration increased while the nitrogen dioxide mole fraction was held constant.

The rate constants obtained in References 9 and 10 were expressed in the form

$$k_8 = A\,(T)^{-3/2}\,\exp\,(-71,800/RT) \qquad\qquad (25)$$

However, in both investigations it was assumed that reaction 10 was very fast so that it effectively doubled the rate of reaction 8. Since our experimental data give an activation energy above 58,000 cal/mole we decided to use the rate constant for reaction 8 as proposed by References 9 and 10. This form of the rate constant agrees with the Rice, Ramsperger, Kassel theory, which predicts this type of temperature dependence for the frequency factor.

Employing only reactions 8, 9, 11 and 12 and the activation energies given by eq. 24 and 25 we obtained as a best fit to our experimental data

$$k_8 = 1.2 \times 10^{22}\,(T)^{-3/2}\,\exp\,(-71,800/RT) \qquad\qquad (26)$$

and

$$k_b = 9 \times 10^{12}\,\exp\,(-25,700/RT) \qquad\qquad (27)$$

However, these expressions did not produce a completely satisfactory fit of the experimental data. Therefore, we must conclude that the mechanism given on page 5 is not complete. The influence of k_9 is contained in the ratio of k_8^* and k_9. If we assume that the activation energy of k_8^* is quite small, then we find the disconcerting result that the activation energy for the rate constant k_9 is -22,000 cal/mole. This negative activation energy clearly indicates that an important step in the reaction mechanism has been overlooked in the analysis. At this point it appears that the only reaction which could possibly be important would be reaction 10; that is, the reaction between atomic oxygen and nitrogen dioxide. However, in the present investigation the role of this step in the reaction could not be ascertained.

It is interesting to compare the results of our study with those of other investigators. The comparison would be most valid in the region of low overall concentration since in this region the effect of k_9 is small. The comparison is given in Table I. From this table we find that the rate constant obtained for reaction 8 is in excellent agreement with that obtained by Huffmann and Davidson and only slightly higher than obtained by Hiraoka and Hardwick. This rate constant, k_8, is obtained by assuming that reaction 10 is very fast, hence producing an observed rate for reaction 8 which is twice as large.

As shown in Table I, the rate constants for reactions 11 and 12 are approximately twice as large as the constants obtained at low temperatures by Rosser and Wise. Furthermore, it is by about a factor of four less than the rate constant obtained by Huffmann and Davidson. The agreement between the results of Rosser and Wise and those presented in this study may be considered

as quite good. It must be remembered that we have extrapolated the results by Rosser and Wise to temperatures twice as high as the temperature of their measurements. Thus, a difference by a factor of only two may be considered as good agreement.

After we had determined the above reaction rates we investigated the effect of the presence of nitrogen dioxide on the dissociation rate of nitrous oxide. Numerous experiments were conducted with various mixtures of argon, nitrous oxide, and nitrogen dioxide. In all of these experiments the decomposition rate of nitrous oxide was not increased. Furthermore, the dissociation rate of nitrogen dioxide also was not changed. Hence, it was concluded that the reaction between atomic oxygen and nitrogen dioxide must be appreciably faster than the corresponding reaction between atomic oxygen and nitrous oxide. In view of these results it is concluded that the atomic oxygen released in the decomposition of nitrogen dioxide cannot be employed to initiate the decomposition process of nitrous oxide.

SECTION VI. THE DECOMPOSITION OF NITROUS OXIDE IN THE

PRESENCE OF OZONE - EXPERIMENTAL RESULTS

The theoretical aspects of the decomposition of nitrous oxide in the presence of ozone has been discussed in Section III. From an experimental viewpoint the choice of the diluent is quite critical. For instance, if oxygen is employed as the diluent, the recombination rate constant is approximately

$$k_{5,O_2} = 10^{15} \text{ cc}^2/\text{mole}^2 - \text{sec} \tag{28}$$

On the other hand if the diluent is argon, the rate constant is approximately

$$k_{5,A} = 10^{14} \text{ cc}^2/\text{mole}^2 - \text{sec} \tag{29}$$

These values have been obtained from Reference 13.

It was decided to employ oxygen as the diluent because of the ease of generating ozone in it. As mentioned earlier, when pure oxygen is used the maximum amount of ozone generated is about 8%. This amount of ozone is desirable from the viewpoint of studying reactions (3) and (4). However, it is marginal in view of the removal of atomic oxygen by reaction (5).

The desired mixture of oxygen, ozone, and nitrous oxide was established on the basis of their partial pressures. Nitrous oxide was admitted to an evacuated 12 liter flask until the desired partial pressure was attained. Pure oxygen then was passed through the ozone generator and into the flask at a fixed flow rate. The percentage of ozone generated in this manner can

be controlled by the oxygen flow rate. The 12 liter flask was filled to a pressure which would yield a final mixture containing two per cent nitrous oxide. If the flask was filled to slightly more than atmospheric pressure, we could fill the shock tube to a pressure of about 100 mm.

The flask was heated on one side with an infrared sunlamp to insure a uniform mixture. The opposite side of the flask was cooled. The resulting convective currents in the flask were sufficient to produce a uniform mixture. This technique was checked by using nitrogen dioxide, instead of nitrous oxide, and filling the flask with oxygen but by-passing the ozone generator. The concentration of nitrogen dioxide was checked over a period of time and also by partially evacuating the flask and withdrawing a sample.

During the experiments with ozone and nitrous oxide a measurement was made of the ozone concentration before and after the gas mixture was introduced into the shock tube. This procedure was followed to check the uniformity of the mixture and to provide two measurements of the concentration as a check on the accuracy of the ozone concentration method discussed in the appendix.

The amount of atomic oxygen behind the front of the shock wave was calculated from equations (6) and (7). The rate of generation of atomic oxygen is given by

$$\frac{d(O)}{dt} = k_6 (M)(O_3) - k_7 (O_3)(O) \tag{28}$$

and the rate of disappearance of ozone is given by

$$\frac{d(O_3)}{dt} = -k_6 (M)(O_3) - k_7 (O_3)(O) \tag{29}$$

The ratio of these two equations yields

$$\frac{d(O_3)}{d(O)} = - \frac{k_6 (M) + k_7 (O)}{k_6 (M) - k_7 (O)} \tag{30}$$

Integrating and denoting the initial conditions by the subscript i, we have

$$\int_{(O_3) = (O_3)_i}^{O} d(O_3) = - \int_{0}^{(O)} \left\{ \frac{k_6 (M) + k_7 (O)}{k_6 (M) - k_7 (O)} \right\} d(O) \tag{31}$$

and thus

$$\frac{-(O_3)_i}{(M)} = \frac{2k_6}{k_7} \ln \left\{ 1 - \frac{k_7}{k_6} \frac{(O)}{(M)} \right\} + \frac{(O)}{(M)} \qquad (32)$$

The atomic oxygen concentration behind the shock front was calculated on the basis of this equation and the calculated thermodynamic properties in the shock-heated gas were based on this concentration ⋅ mixtures containing two per cent nitrous oxide. The remainder of the mix. ⋅re was molecular oxygen. It is assumed that the gas is in complete thermodynamic equilibrium.

To accurately determine the rate of the reaction between atomic oxygen and nitrous oxide two sets of experiments were conducted. In the first set of experiments the rate of decomposition of nitrous oxide in molecular oxygen was determined for a given gas concentration. Identical experiments then were conducted but with a small percentage of ozone. The experimental results are given in Figure 6. It is obvious from these experiments that the decomposition rate of nitrous oxide is accelerated in the presence of atomic oxygen.

If we consider only reactions (1) - (4) and rewrite these as

$$N_2O + M \xrightarrow{k_{33}} N_2 + O + M \qquad (33)$$

$$N_2O + O \xrightarrow{k_{34}} N_2 + O_2 \quad \text{or} \quad 2NO \qquad (34)$$
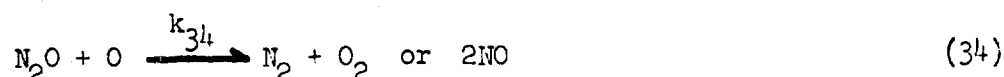
then the rate of decomposition of nitrous oxide is given by

$$\frac{d}{dt} (N_2O) = -k_{33} (N_2O)(M) \left\{ 1 + \frac{k_{34}}{k_{33}} \frac{(O)}{(M)} \right\} = -K_{exp} (N_2O) \qquad (35)$$

The rate constant k_{33}, was determined in a set of control experiments. Thus, to determine the extent to which atomic oxygen affects the reaction rate we need only investigate the second term on the right hand side of equation 35.

A first approximation to the rate constant k_{34} can be obtained from the low temperature data of Kaufman, Gerri, and Bowman (Ref. 14). According to their data we have

$$k_3 = 3 \times 10^{10} \exp (-14,500/RT) \qquad (36)$$

$$k_4 = 10^{11} \exp(-15,500/RT) \tag{37}$$

However, according to Fenimore and Jones (Ref. 16), the combined rate constant is

$$k_{34} = 10^{14} \exp(-28,000/RT) \tag{38}$$

At $1800^\circ K$, k_{34} from equation (38) produces a rate 20 times faster than the combined rate constants $k_3 + k_4$.

According to equation (35) the rate constant k_{34} can be expressed in terms of K_{exp} and k_{33} as follows:

$$k_{34} = \frac{1}{(O)}(K_{exp} - k_{33}(O_2)) \tag{39}$$

The atomic oxygen concentration is calculated from equation (32). The values of k_{34} calculated by means of equations (39) and (32) are shown in Figure 7. For comparison purposes, the extrapolated rate constant of Kaufman, Gerri, and Bowman (Ref. 14), and that of Fenimore and Jones (Ref. 16) are shown.

Our data indicate a pronounced effect of pressure on the reaction between atomic oxygen and nitrous oxide. To insure that this effect was not due to the recombination of the atomic oxygen we assumed one of the largest values quoted for k_5 in the literature ($k_5 = 10^{15}$ $cc^2/mole^2$. sec)(Ref. 17) and calculated the rate of change of atomic oxygen as the decomposition process proceeded. We found that in the temperature range of interest ($1660^\circ K - 2100^\circ K$) the recombination of atomic oxygen is completely negligible when $(M) = 0.35 \times 10^{-5}$ and 0.71×10^{-5} moles/cc. At the highest gas concentration, $(M) = 1.41 \times 10^{-5}$ moles/cc, and at high concentrations of atomic oxygen we found that the recombination of atomic oxygen is of marginal importance at the lower temperatures but is negligible at the higher temperatures. Another indication that recombination does not affect our results is given by our observation that the rate constant, k_{34} obtained for the same total gas concentration is not a function of the relative concentration of atomic oxygen.

The amount of experimental scatter in the values of k_{34} given in Figure 7 is to be expected, since they are obtained by a difference of experimentally determined rate constants (equation 39). Hence, inaccuracies in the values of K_{exp} become magnified in k_{34}.

After observing the effect of pressure on the reaction between atomic oxygen and nitrous oxide, we propose the following scheme:

$$N_2O + O \underset{k_{-40}}{\overset{k_{40}}{\rightleftharpoons}} N_2O_2 \tag{40}$$

$$N_2O_2 + M \xrightarrow{k_{41}} M + N_2O + O \tag{41}$$

$$N_2O_2 \xrightarrow{k_{42}} 2NO \text{ (or } N_2 + O_2) \tag{42}$$

where N_2O_2 is a reaction intermediate. When these reactions are combined with the reaction as descibed by equation (33) we arrive at

$$\frac{d(N_2O)}{dt} = - k_{33}(N_2O)(M) - k_{40}(N_2O)(O) + k_{-40}(N_2O_2) \tag{43}$$

$$+ k_{41}(N_2O_2)(M)$$

Assuming a steady-state concentration of N_2O_2, we have

$$N_2O_2 = \frac{k_{40}(N_2O)(O)}{k_{41}(M) + k_{42} + k_{-40}} \tag{44}$$

which yields

$$\frac{d(N_2O)}{dt} = - k_{33}(N_2O)(M) - \frac{k_{42} k_{40}(N_2O)(O)}{k_{41}(M) + k_{42} + k_{-40}} \tag{45}$$

If we assume that $k_{41}(M) \gg k_{42} + k_{-40}$ we obtain

$$\frac{d(N_2O)}{dt} = - k_{33}(N_2O)(M) - \frac{k_{42} k_{40}}{k_{41}(M)}(N_2O)(O) \tag{46}$$

From this expression we find that consideration of reactions (40), (41), and (42) produces the observed effect of pressure. In fact, when comparing this expression with equation 35, we find that $k_{34} = k_{42} k_{40}/k_{41}(M)$. Thus to obtain the quantity $k_{42} k_{40}/k_{41}$ we need only multiply the observed values of k_{34} by the total gas concentration (M). The results are shown in Figure 8 together with the results of Fenimore and Jones which were multiplied by the total gas concentration. Fenimore and Jones employed flames at pressures between 6 cm and 10 cm. To reduce their data we assumed that all their flames were burned at a pressure of 10 cms. Also shown in Figure 8 is the estimated

value of Bradley and Kistiakowsky reduced in the same manner. Figure 8 shows that the agreement between the different measurements is quite good. No attempt has been made at adapt the data of Kaufman, Gerri, and Bowman.

If we assume that only reaction (40) has an activation energy, we find that $k_{40} = A \exp (-29,000 \pm 4000/RT)$ and

$$\frac{k_{40} \, k_{42}}{k_{41}} = 1.4 \times 10^8 \exp (-29,000/RT) \tag{47}$$

To determine the collision factor for k_{40} we must assume some value for k_{42}/k_{41}. This value may be obtained by assuming that $k_{41} (M)/k_{42}$ is much larger than unity at the lowest concentration at which measurements were made. Employing the total gas concentration of Fenimore and Jones we find that

$$\frac{k_{41}}{k_{42}} > \frac{1}{0.89 \times 10^{-6}} = 1.1 \times 10^6$$

Thus, a reasonable value of k_{41}/k_{42} amounts to approximately 5×10^6. Assuming no temperature dependence of k_{41}/k_{42}, we find that $k_{40} = 2.7 \times 10^{11}$ at $1850^\circ K$. This leads to a value for the collision factor of about 7.1×10^{14}. Thus

$$k_{40} = 7.1 \times 10^{14} \exp (-29,000/RT) \text{ cc/mole. sec}$$

If we consider the results of Kaufman, Gerri, and Bowman (Ref. 14) and include our step involving the reaction intermediate, we obtain an equation for the initial generation of nitric oxide almost identical to theirs. At $973^\circ K$ we obtain from the data of Kaufman, et. al. $k_{41}/k_{40} \, k_{42} = 0.055$. From our expression for $k_{40} \, k_{42}/k_{41}$ we find that the extrapolation to $973^\circ K$ yields $k_{41}/k_{42} \, k_{40} = 0.032$ in good agreement with that of Kaufman, et. al.

In view of the agreement between the results of Fenimore and Jones who measured the rate of increase of the nitric oxide concentration and our results based only on the accelerated rate of decomposition of nitrous oxide in the presence of atomic oxygen, we believe that reaction 4 dominates reaction 3 considerably. This conclusion is also supported by the results of Kaufman, et. al. (Ref. 14). It is somewhat surprising that this condition exists in view of the larger energy release of reaction 3. It is possible that this condition exists because the atomic oxygen in the ground state nitrous oxide molecule is in a (^1D) state.

SECTION V. CONCLUSIONS

We have shown that the assumption of a reaction intermediate in the reaction between atomic oxygen and nitrous oxide explains the disagreement between the rate constants obtained by various investigators and the rate constants obtained in our experiments. Although the reaction mechanism proposed by the authors is verified by experimental data we do not feel that the actual details of the reaction have been explained completely.

The decomposition of nitrogen dioxide is such that the atomic oxygen released in the initial step reacts very rapidly with the remaining nitrogen dioxide and consumes atomic oxygen quite fast. In fact, the reaction between atomic oxygen and nitrogen dioxide is much faster than the corresponding reaction between atomic oxygen and nitrous oxide. Furthermore, the use of nitrogen dioxide is open to criticism in view of the fact that one of the major products of the decomposition of nitrogen dioxide is nitric oxide, an undesirable species in wind tunnels.

On the basis of the data collected during this study, it appears highly unlikely that the decomposition process may be initiated by the addition of either ozone or nitrogen dioxide. The major difficulty associated with the use of ozone is the fact that the ozone must be heated to temperatures of approximately $1500^{\circ}K$ before the amount of atomic oxygen liberated during the ozone decomposition.

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APPENDIX A

DETERMINATION OF OZONE CONCENTRATION

According to Treadwell (Ref. 15) the amount of ozone in a gaseous system may be determined by the following procedure. First, a known portion of the gas is passed through a double normal potasium iodide solution. Next, an equal portion of double normal sulfuric acid is added to the potasium iodide solution. The solution becomes brownish in color. Then, a 0.1 normal sodium thiosulfate solution is slowly added to the mixture of potasium iodide and sulfuric acid until the mixture becomes colorless. Just near the end of the titration process a small amount of starch solution may be added to accentuate the color transition of the mixture.

From the known amount of sodium thiosulfate and the fact that 1 ml of 0.1 sodium thiosulfate indicates 0.0024 grams of ozone we may determine the percentage of ozone in the system. In our particular experimental configuration we determined the amount of gas passed through the potasium iodide solution. This amount of gas is obtained by measurement of the pressure of the gas within a known volume before and after a sample has passed through the potasium iodide solution. From the equation a state for an ideal gas

$$pV = nRT \qquad\qquad \text{A-1}$$

where p is the pressure, V the known volume, R the universal gas constant, T the temperature and n the number of moles of gas in the volume V. Thus

$$\Delta p = \Delta n \; \frac{RT}{V} \qquad\qquad \text{A-2}$$

where Δp is the difference of pressure before and after. For the ozone

$$\Delta p_{O_3} = \Delta n_{O_3} \; \frac{RT}{V} \qquad\qquad \text{A-3}$$

and the percentage of ozone in the system is

$$\% \; O_3 \; (\text{volume}) = \frac{\Delta p_{O_3}}{\Delta p} \; (100) = \frac{\Delta n_{O_3}}{\Delta n} \; (100) \qquad\qquad \text{A-4}$$

From equation A-2

$$\% \ O_3 \ (volume) = \left(\frac{\Delta n_{O_3} \ RT}{\Delta p \ V} \right) (100) \qquad \text{A-5}$$

the mass of ozone passing through the potasium iodide solution would be

$$M_{O_3} = (\Delta N)(0.0024) \text{gms} = \Delta n_{O_3} \ m_{O_3} \qquad \text{A-6}$$

where ΔN is the number of ml of sodium thiosulfate used in the titration process. Therefore,

$$\% \ O_3 \ (volume) = \left(\frac{\Delta N \ (0.0024) \ RT}{\Delta p \ V \ m_{O_3}} \right) (100) \qquad \text{A-7}$$

TABLE I

Comparison of Reaction Rate Constants

REACTION	SOURCE	RATE CONSTANT
$NO_2 + NO_2 \longrightarrow 2NO + O_2$ And	Rosser and Wise (Ref. 12)	$4.1 \times 10^{12} \exp(-25,700/RT)$
$NO_2 + NO_2 \longrightarrow NO_3 + NO$	Huffman and Davidson (Ref. 9)	$2.5 \times 10^{13} \exp(-25,000/RT)$
(Combined Rate)	Fishburne, Bergbauer and Edse	$9 \times 10^{12} \exp(-25,700/RT)$
$NO_2 + M \longrightarrow NO + O + M$ And	Huffman and Davidson (Ref. 9)	$1.2 \times 10^{22} (T)^{-3/2} \exp(-72,000/RT)$
$NO_2 + O \longrightarrow NO + O_2$	Hiraoka and Hardwick (Ref. 10)	$9.4 \times 10^{21} (T)^{-3/2} \exp(-72,000/RT)$
(Combined Rate)	Fishburne, Bergbauer and Edse	$1.2 \times 10^{22} (T)^{-3/2} \exp(-71,800/RT)$

ELECTRODES

CuSO$_4$ SOLUTION

RUBBER SEAL

COOLING WATER OUT

COOLING WATER IN

WATER JACKET

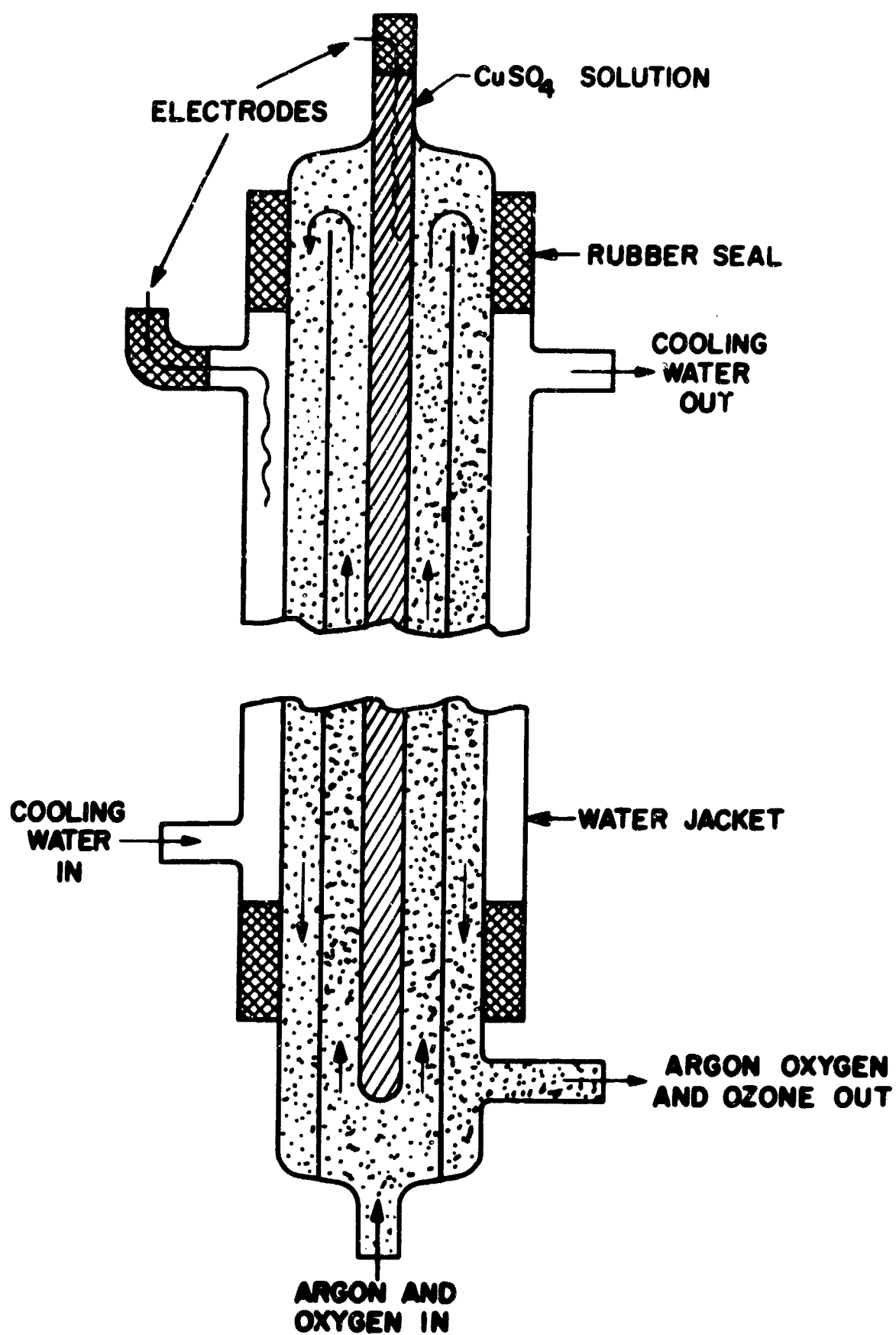ARGON OXYGEN AND OZONE OUT

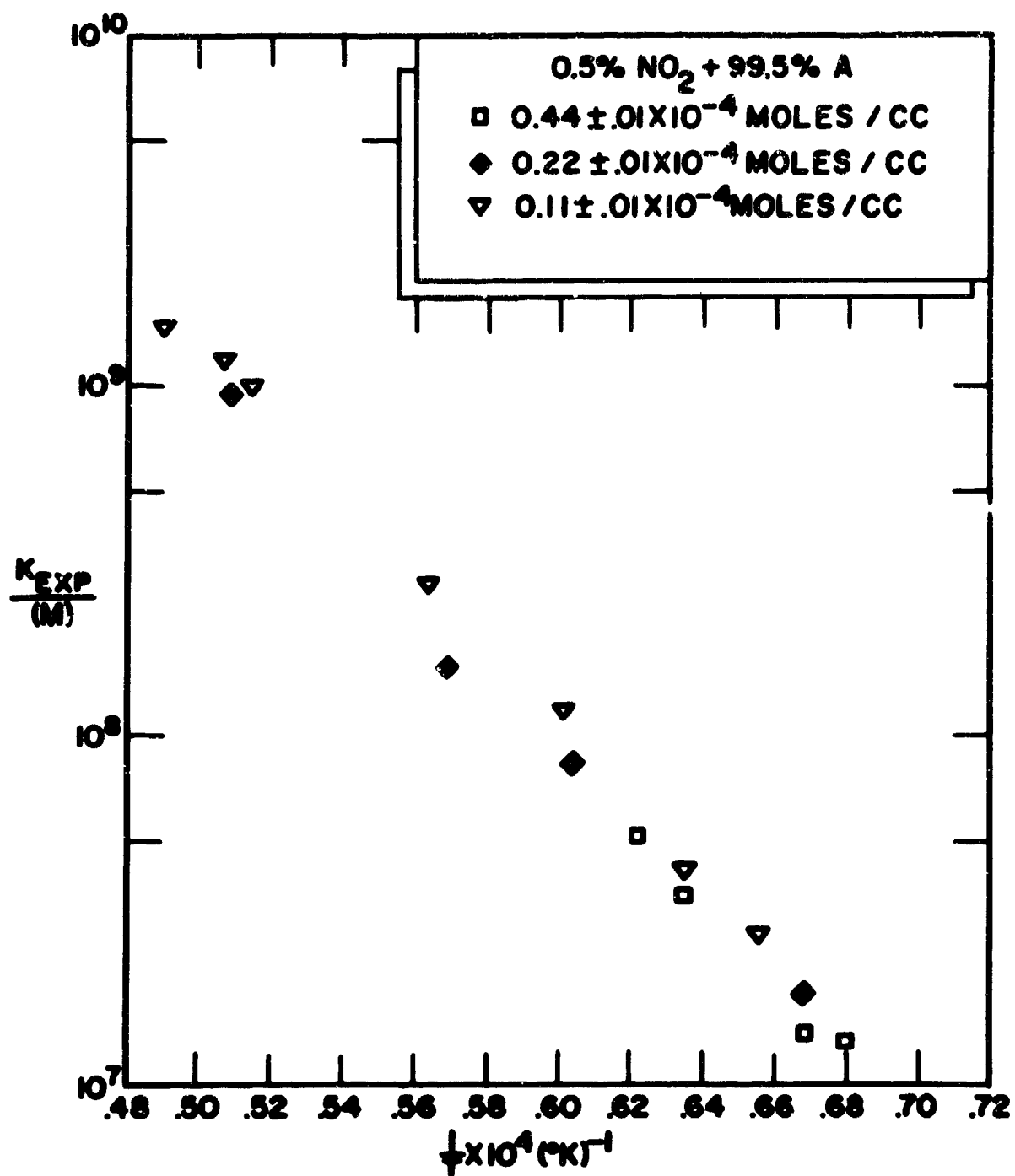ARGON AND OXYGEN IN

FIGURE I   OZONE GENERATOR

FIGURE 2. EXPERIMENTAL REACTION RATE CONSTANT
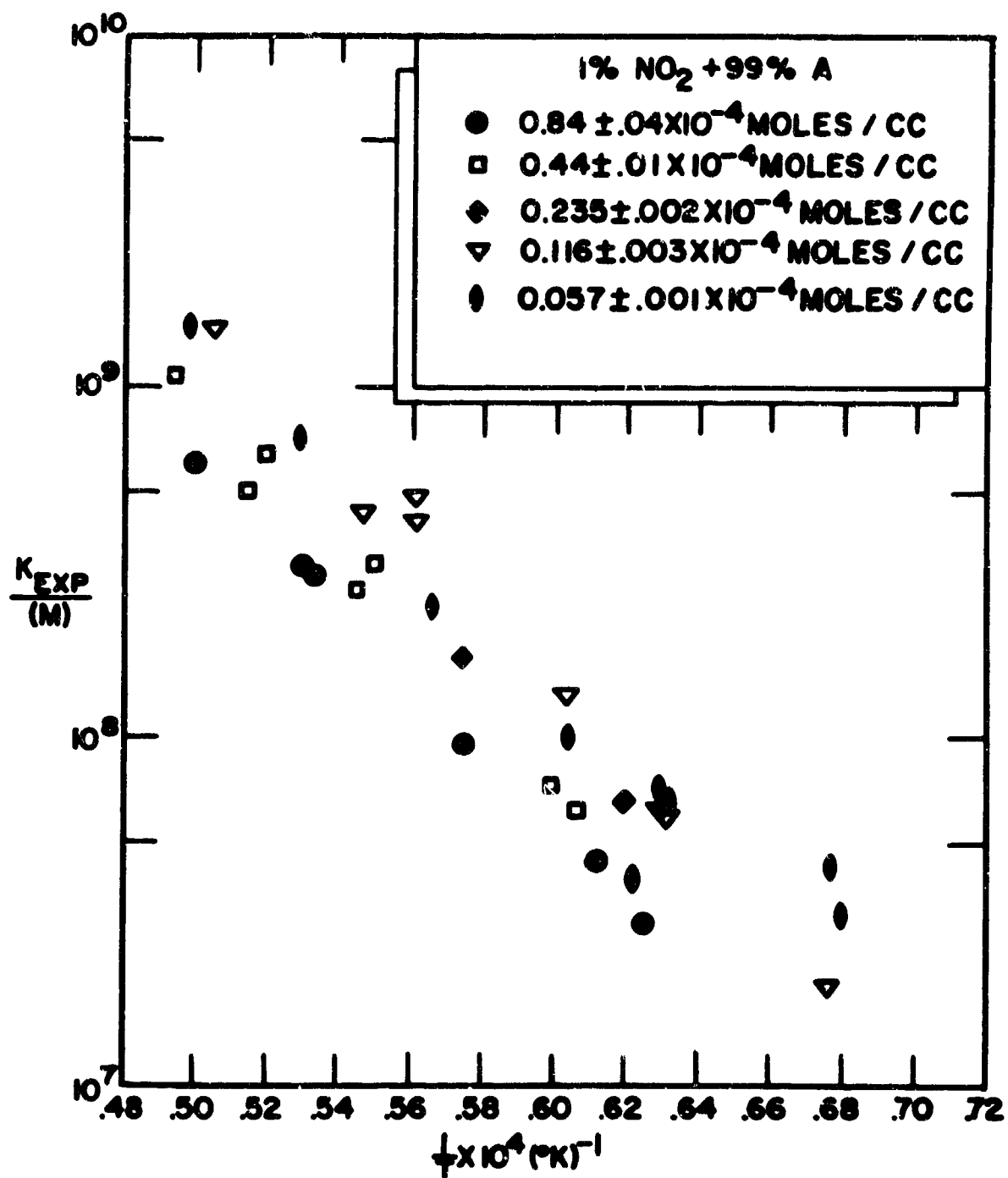FOR 0.5% NO_2 +99.5% ARGON

FIGURE 3. EXPERIMENTAL REACTION RATE CONSTANT
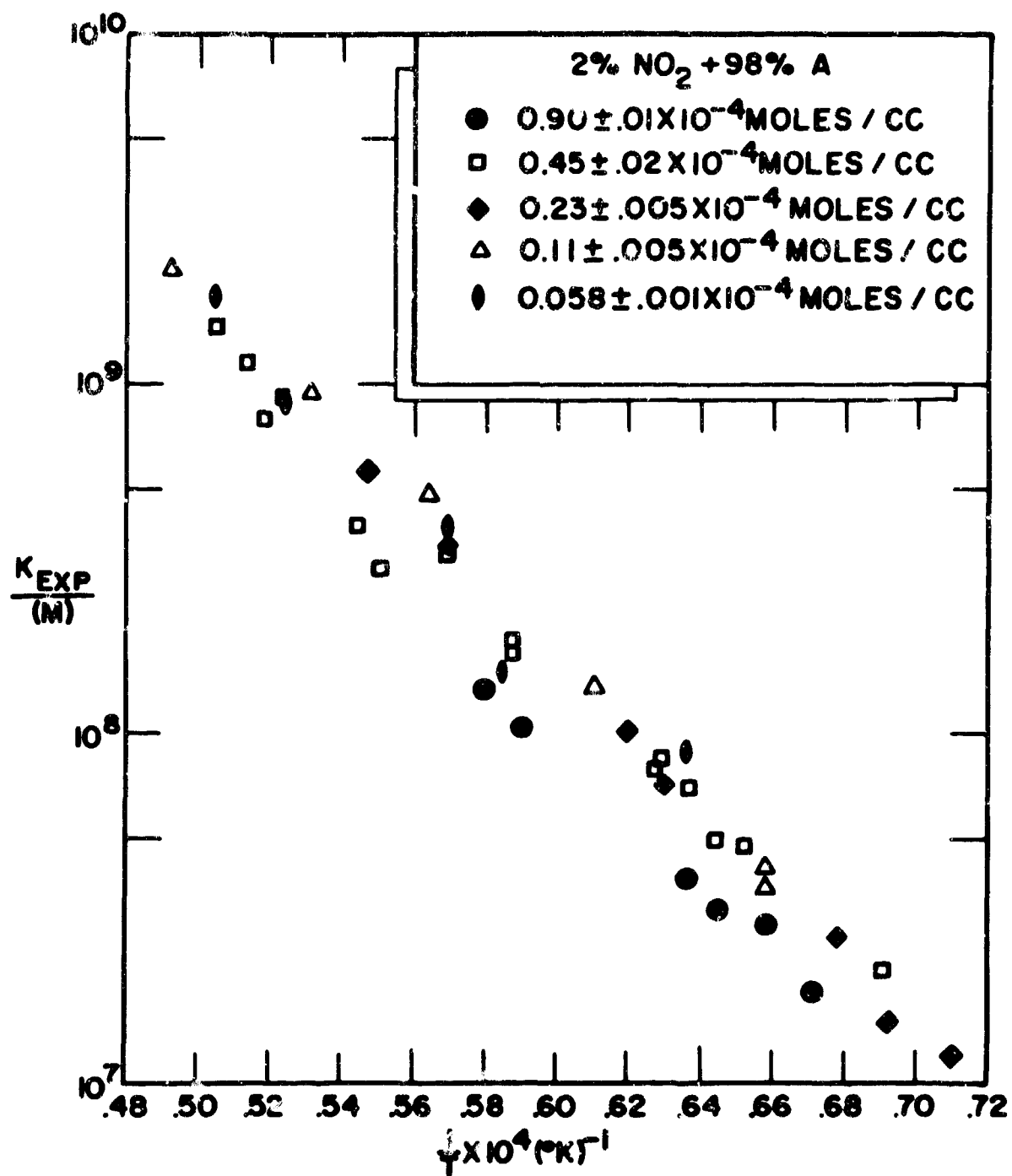FOR 1% NO_2 +99% ARGON

FIGURE 4. EXPERIMENTAL REACTION RATE CONSTANT
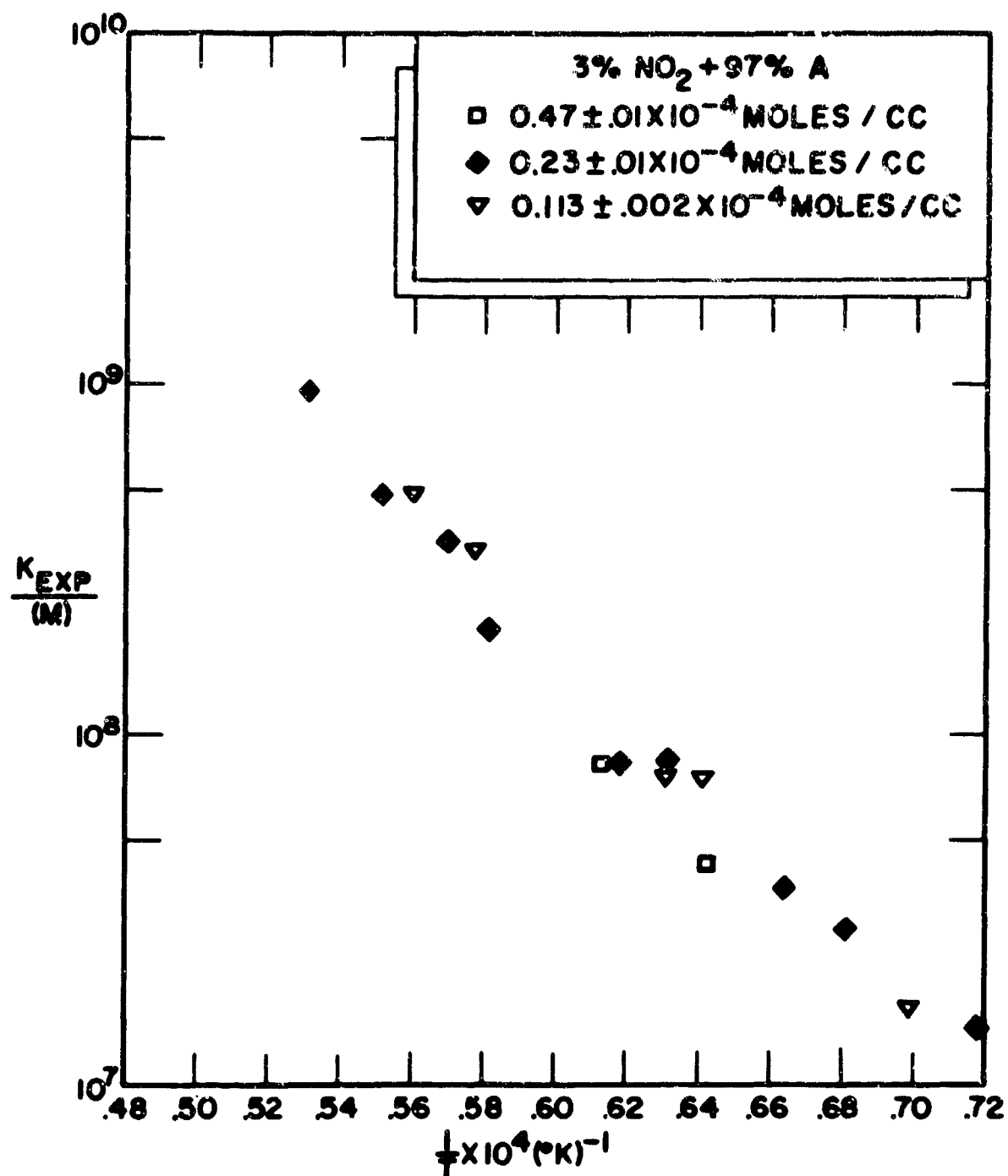FOR 2% NO_2 + 98% ARGON

FIGURE 5. EXPERIMENTAL REACTION RATE CONSTANT
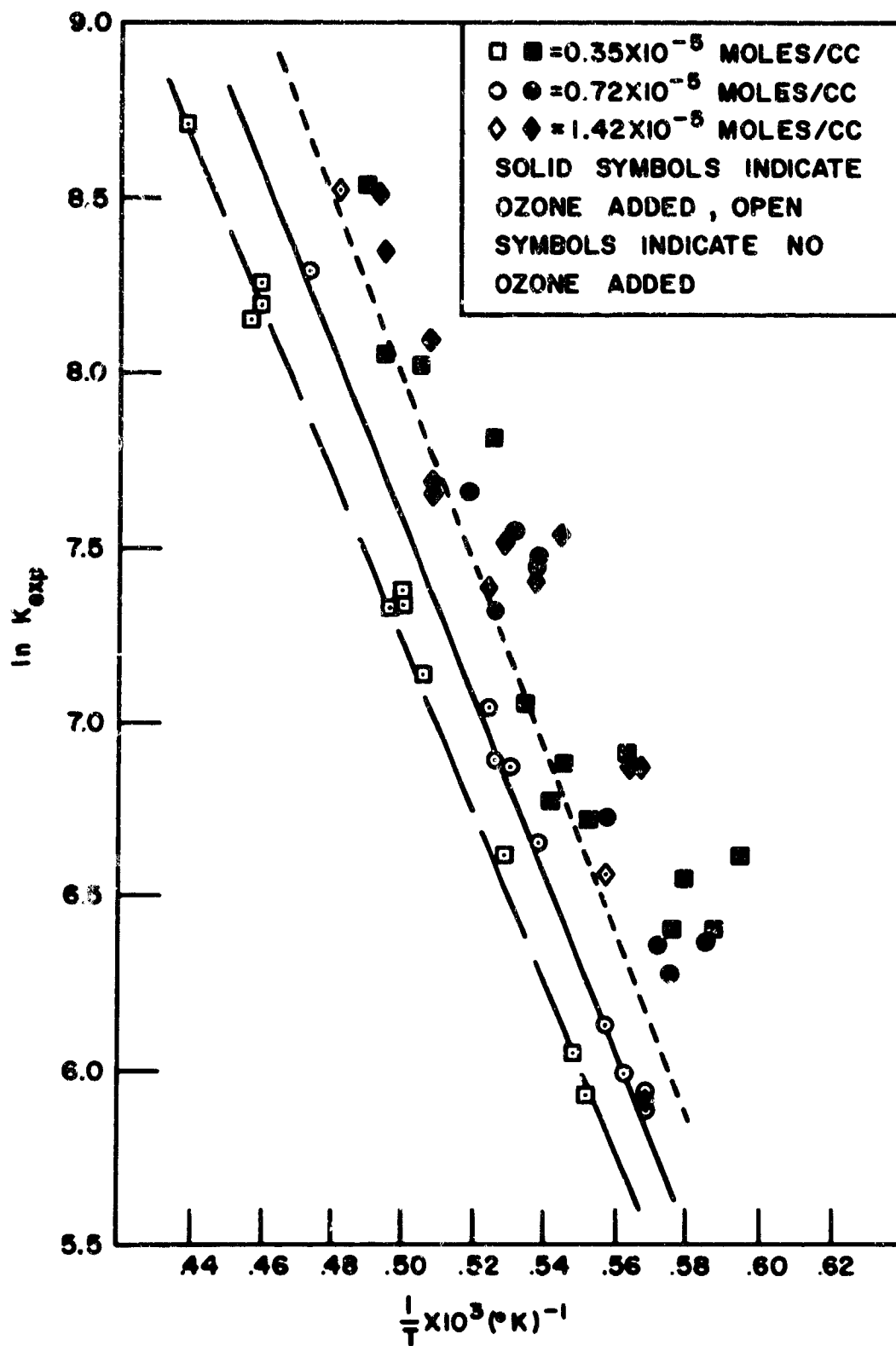FOR 3% NO_2 + 97% ARGON

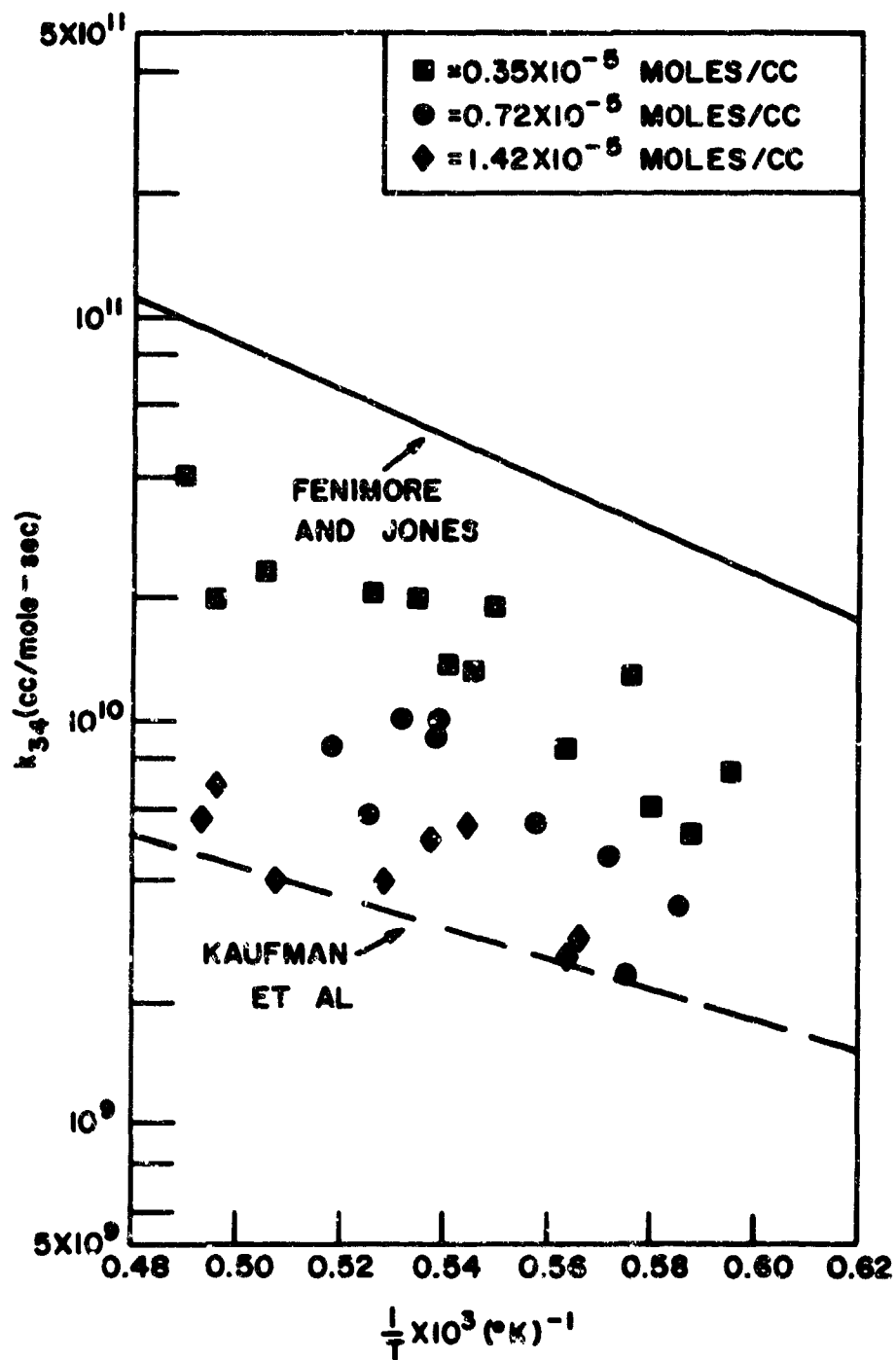FIG.6 – EFFECT OF ATOMIC OXYGEN ON THE DECOMPOSITION OF NITROUS OXIDE.

FIG.7—RATE CONSTANT FOR THE REACTION BETWEEN
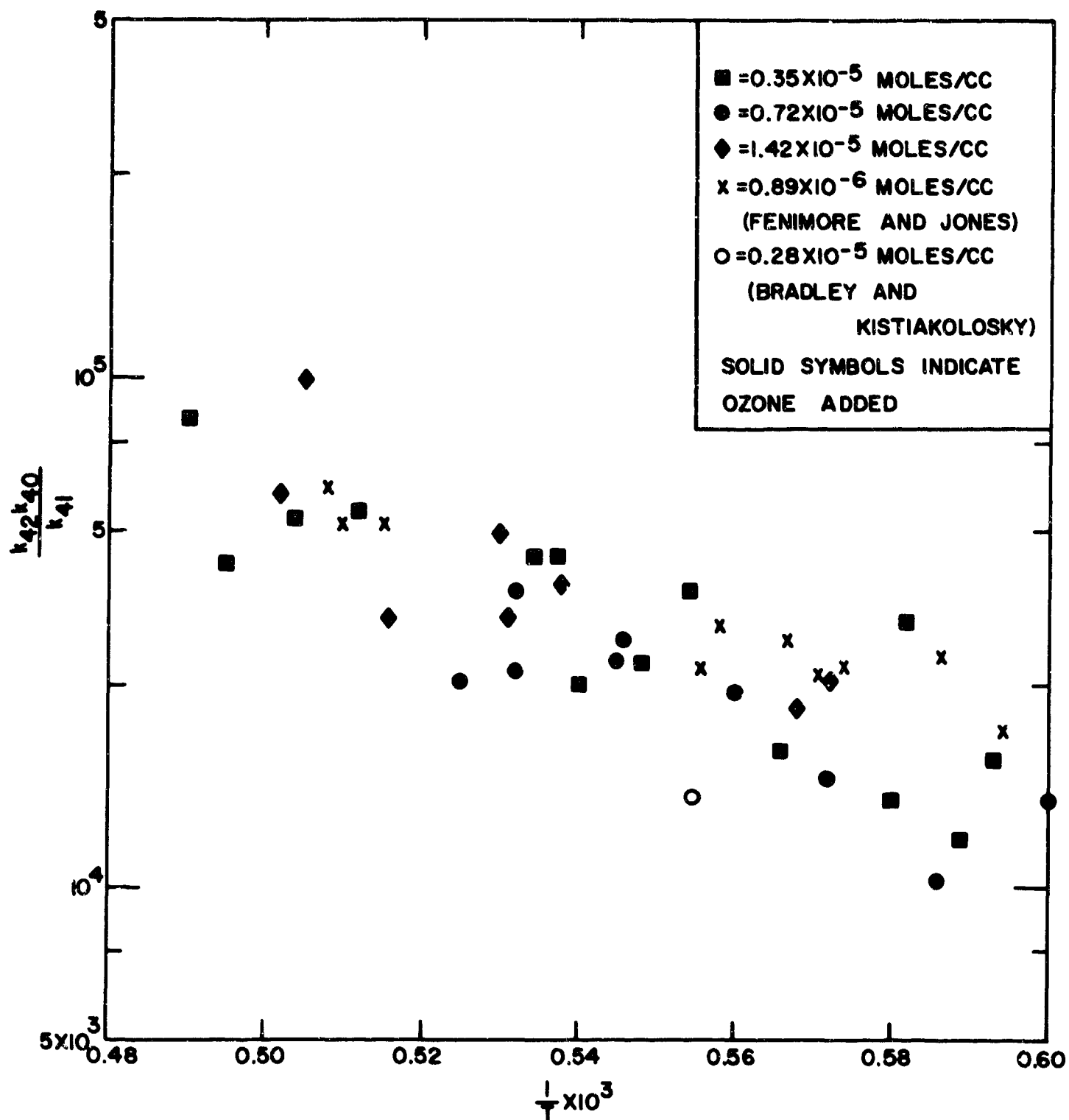ATOMIC OXYGEN AND NITROUS OXIDE.

FIG.8-REDUCED REACTION RATE CONSTANT FOR THE REACTION BETWEEN ATOMIC OXYGEN AND NITROUS OXIDE.

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13. ABSTRACT The reaction between atomic oxygen and nitrous oxide has been studied at temperatures ranging from $1500^\circ K$ to $2100^\circ K$. The atomic oxygen in this study was generated by either the thermal decomposition of nitrogen dioxide or the thermal decomposition of ozone. To determine the amount of atomic oxygen released in the thermal decomposition of nitrogen dioxide it was necessary to study this decomposition in detail. This study was conducted also at temperatures ranging from $1500^\circ K$ to $2000^\circ K$ and over a wide range of concentrations and pressures. The reaction rates obtained for the various steps in the decomposition of nitrogen dioxide are in general agreement with those obtained by other investigators. The reaction of nitrous oxide in the presence of nitrogen dioxide with argon as the diluent was studied to determine if the oxygen released in the decomposition of nitrogen dioxide would accelerate the decomposition of nitrous oxide. No noticable acceleration was observed. Many experiments were conducted with a nitrous oxide mole fraction of 0.02 and ozone mole fractions varying between 0.005 and 0.06. In these experiments the diluent was molecular oxygen. The presence of atomic oxygen definitely produced an increase in the rate of decomposition of nitrous oxide. It is found that the reaction between atomic oxygen and nitrous oxide is pressure dependent. It is shown that the different rate constants obtained by other investigators may be reasonably explained on the basis of a pressure dependent step in the reaction mechanism.

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